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PATENT

S-2476

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of: Michio TANIMOTO, et al.

Serial No.: 09/729,433

Group: 1755

Filed: December 5, 2000

Examiner:

For: COMPLEX OXIDE CATALYST AND PROCESS FOR PREPARATION OF
ACRYLIC ACID

April 3, 2001

The Honorable Commissioner of Patents
and Trademarks
Washington, D.C. 20231

REQUEST FOR PRIORITY

Sir:

Applicants in order to perfect their claim to priority of their corresponding Japanese Application Serial No. 349,067/99 filed August 12, 1999, are herewith submitting a certified copy of the Japanese priority application together with a certified English text translation of the priority application.

Respectfully submitted,

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VERIFICATION OF TRANSLATION

In the matter of Application for
Letters Patent by Michio TANIMOTO, et al.
U. S. Serial No.: Unassigned
Filed: December 4, 2000
For: COMPLEX OXIDE CATALYST AND PROCESS FOR PREPARATION OF
ACRYLIC ACID

I, Asako TSUKAMOTO, a translator of Odajima & Co., Nippon Jitensha Bldg.,
9-15, Akasaka 1-chome, Minato-ku, Tokyo, Japan, declare:

That I am thoroughly conversant with both the Japanese and English languages;

That the attached translation is a true translation into English of the certified copy
of Japanese patent application No. 349,067/99 filed on December 8, 1999.

I further declare that all statements made herein of my own knowledge are true
and that all statements made on information and belief are believed to be true; and
further that these statements are made with the knowledge that willful false statements
and the like so made are punishable by fine or imprisonment, or both, under Section
1001 of Title 18 of the United States Code, and that such willful false statements may
jeopardize the validity of the application or any patent issuing thereon.

Signed this 8th day of February, 2001


Asako TSUKAMOTO

39/806770

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(TRANSLATION)

PATENT OFFICE
JAPANESE GOVERNMENT

This is to certify that the annexed is a true copy of the following
application as filed with this Office.

Date of Application : December 8, 1999

Application Number: Patent Application No. 349067/99

Applicant(s) : Nippon Shokubai Co., Ltd.

January 26, 2001

Kozo OIKAWA

Commissioner,
Patent Office

Certification Number 3001154/2001

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[Reference Number] K0006905

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[International Patent Classification] C07C 57/05

[Title of the Invention] Complex Oxide Catalyst and Process for
Preparation of Acrylic Acid

[Number of Claims] 5

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[Document Name] SPECIFICATION

[Title of the Invention] Complex Oxide Catalyst and Process for
Preparation of Acrylic Acid

[Claims]

- 5 [Claim 1] Complex oxide catalyst which is expressed by the following
general formula (1):



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15

20

25

(in which Mo is molybdenum; V is vanadium, W is tungsten, Cu is copper, A is at least an element selected from antimony, niobium and tin; B is at least an element selected from alkaline earth metals; C is at least an element selected from silicon, aluminum, titanium and zirconium; D is at least an element selected from phosphorus, tellurium, cerium, lead, arsenic and zinc; E is at least an element selected from Group IA and Group IIb elements of the periodic table, boron, iron, bismuth, cobalt, nickel and manganese; and O is oxygen; a, b, c, d, e, f, g, h, i and x denote the atomic ratios of Mo, V, W, Cu, A, B, C, D, E and O, respectively; and where $a = 12$, $2 \leq b \leq 15$, $0 \leq c \leq 10$, $0 < d \leq 6$, $0 \leq e \leq 6$, $0 < f \leq 10$, $0 < g \leq 10$, $0 \leq h \leq 5$, $0 \leq i \leq 5$, and x is a numerical value determined by the extents of oxidation of the other elements)

which is characterized in that a compound containing the components B and C is used as at least a part of the supply sources of components B and C at the time of the catalyst preparation.

- 30 [Claim 2] A complex oxide catalyst as described in Claim 1, in which
the component B is at least an element selected from magnesium, calcium, strontium and barium.

[Claim 3] A complex oxide catalyst as described in Claim 1 or 2, in

which the component C is at least an element selected from silicon and aluminum.

[Claim 4] A complex oxide catalyst as described in any one of Claims 1 - 3, in which the compound containing the components B and C is
5 heat-treated at 500 - 2000°C.

[Claim 5] A process for preparing acrylic acid which comprises vapor-phase catalytic oxidation reaction for producing acrylic acid through oxidation of acrolein at vapor phase with molecular oxygen or a molecular oxygen-containing gas, which is characterized in that said
10 reaction is conducted in the presence of the complex oxide catalyst of Claim 1.

[Detailed Explanation of the Invention]

[0001]

15 [Field of industrial utilization]

This invention relates to complex oxide catalysts and production process of acrylic acid. More particularly, the invention relates to complex oxide catalysts suitable for use in producing acrylic acid from acrolein by vapor-phase catalytic oxidation reaction, and to a
20 producing process of acrylic acid from acrolein using said catalysts.

[0002]

[Prior Art]

A large number of improved catalysts for preparing acrylic acid through vapor phase catalytic oxidation of acrolein have been
25 proposed. For example, Japanese Patent Publication No. 12129/69 described a catalyst formed of molybdenum, vanadium and tungsten; Publication No. 11371/74, that formed of molybdenum, vanadium, copper, tungsten and chromium; Publication No. 25914/75, that formed of molybdenum and vanadium; and Laid-open (Kokai) Application,
30 Kokai No. 85091/77, that formed of molybdenum, vanadium, copper and at least one element of antimony and germanium.

[0003]

However, these conventional catalysts are not fully satisfactory for industrial working, for such defects that the yield of the object product, i.e., acrylic acid, is insufficient and deterioration
5 rate in activity is high, leading to short catalyst life. Therefore, it is necessary to develop catalysts which excel in stability and enable acrylic acid production at high yield over prolonged periods.

[0004]

The applicant has disclosed the catalysts containing
10 molybdenum, vanadium and alkaline earth metals in Kokai Application, Kokai No. 117419/74, which catalysts, however, are still open to improvements in respect of acrylic acid yield and catalyst life.

[0005]

[Problems to be solved by the invention]

15 One of the objects of the present invention is to provide complex oxide catalysts, in particular, those which are suitable for producing acrylic acid through vapor phase catalytic oxidation of acrolein.

[0006]

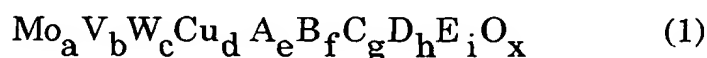
20 Another object of the present invention is to provide a process for preparing acrylic acid at high yield over prolonged periods, by oxidizing acrolein in the presence of catalyst at vapor phase with molecular oxygen or a molecular oxygen-containing gas.

[0007]

25 [Means to solve the problems]

We have discovered that catalysts excelling in activity, selectivity and also catalyst life and which exhibit stable performance over prolonged periods can be obtained in the occasion of preparing a complex oxide catalysts expressed by the following general formula (1):

30

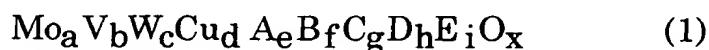


(in which the components and their ratios are as later identified),

when a compound containing both components B and C is used as at least a part of supply sources of components B and C; and that the use of this catalyst enables production of acrylic acid from acrolein at high yield over prolonged periods. Based on these discoveries the present invention is completed.

[0008]

Namely, the present invention relates to a complex oxide catalyst which is expressed by the following general formula (1):



15

(in which Mo is molybdenum; V is vanadium, W is tungsten, Cu is copper, A is at least an element selected from antimony, niobium and tin; B is at least an element selected from alkaline earth metals; C is at least an element selected from silicon, aluminum, titanium and zirconium; D is at least an element selected from phosphorus, tellurium, cerium, lead, arsenic and zinc; E is at least an element selected from Group IA and Group IIb elements of the periodic table, boron, iron, bismuth, cobalt, nickel and manganese; and O is oxygen; a, b, c, d, e, f, g, h, i and x denote the atomic ratios of Mo, V, W, Cu, A, B, C, D, E and O, respectively; and where $a = 12$, $2 \leq b \leq 15$, $0 \leq c \leq 10$, $0 < d \leq 6$ (preferably $0.05 \leq d \leq 6$), $0 \leq e \leq 6$, $0 < f \leq 10$ (preferably $0.01 \leq f \leq 10$), $0 < g \leq 10$ (preferably $0.01 \leq g \leq 10$), $0 \leq h \leq 5$, $0 \leq i \leq 5$, and x is a numerical value determined by the extents of oxidation of the other elements)

30

which is characterized in that a compound containing the components

B and C is used as at least a part of the supply sources of components B and C at the time of the catalyst preparation.

The invention also relates to a process for preparing acrylic acid by vapor phase catalytic oxidation reaction comprising oxidizing acrolein at vapor phase with molecular oxygen or a molecular oxygen-containing gas to produce acrylic acid, which is characterized in that said reaction is conducted in the presence of aforesaid complex oxide catalyst.

[0009]

10 [Embodiments of the invention]

Those complex oxide catalysts which are represented by the general formula (1) are per se known as disclosed in said Kokai No. 117,419/74. In the complex oxide catalysts of the invention, preferably antimony and tin are used as the component A; magnesium, calcium, strontium and barium, as the component B; silicon and aluminum, as the component C; phosphorus, tellurium and zinc; as the component D; sodium, potassium, iron, cobalt, nickel and boron, as the component E; respectively.

[0010]

20 The characteristic feature of the invention lies in the use of a compound containing both components B and C (which is hereafter conveniently referred to as a B/C components - containing compound) as at least a part of supply sources (starting compounds) of components B and C in the occasion of preparing the complex oxide catalysts of the present invention. The reason why the complex oxide catalysts of excellent performance are obtained through such a practice is not yet clear. At the present time we presume that whereby improved stability of the component B contributes to the better performance, while the scope of this invention should never be
30 restricted by this presumption.

[0011]

The ratio of a B/C components - containing compound in the supply sources of components B and C (i.e., total volume of the starting materials) is 0.5/1 to 1/1, preferably 0.8/1 to 1/1, in terms of the atomic ratio. In particular, it is preferred to supply the total amount of the component B by a B/C components - containing compound.

[0012]

As the supply sources for Mo, V, W, Cu, components A, D and E; any compounds which contain the named individual elements and which produce the corresponding oxides upon calcination can be used.

[0013]

As B/C components - containing compounds, any of marketed compounds which contain both components B and C can be used as they are, while they are normally used in the form of an oxide (B/C components - containing oxide). This B/C components - containing oxide can be prepared through, for example, the following procedures: ① use of a component B - containing compound and a component C - containing compound as the starting materials; dissolve or disperse these compounds in water, remove the water content, give subsequent treatment(s) such as drying, and thereafter conduct a heat-treatment, preferably at temperature of 500-2000°C; ② thoroughly mix a component B - containing oxide with a component C - containing oxide and heat-treat the mixture at temperatures of, preferably 500-2000°C; ③ heat-treat a B/C components - containing compound at temperatures of, preferably, 500-2000°C.

[0014]

Said B/C components - containing compounds are preferably used in pulverized state to an average particle diameter of not greater than 200 μm , more advantageously not greater than 100 μm , and most advantageously, not greater than 50 μm .

[0015]

Where either of the components B and C comprises more than one element, it can be used for the B/C components - containing compound as to at least one of the elements. The B/C components -
5 containing compound may also be caused to contain a component other than the components B and C, e.g., component E, to let it serve also as a supply source of the component E.

[0016]

The complex oxide catalysts of the invention can be
10 prepared by the methods generally practiced for preparing this kind of complex oxide catalysts, except that a B/C components - containing compound is used as at least a part of the supply sources of the components B and C.

[0017]

15 Shape of the complex oxide catalysts of the invention is not critical, which may be any optional forms such as ring, sphere, column, tablet and the like, with an average diameter of 1-15 mm, preferably 3-10 mm. In that occasion, those well known additives for their effect of improving the strength and attrition resistance of catalysts, such as
20 inorganic fibers, e.g., glass fiber or various whiskers may be added. Also for controlling the catalyst properties with good reproducibility, additives such as ammonium nitrate, cellulose, starch, polyvinyl alcohol, stearic acid and the like may be used.

[0018]

25 While the complex oxide catalysts of the invention are each useful by itself, they are preferably used in the form supported on inert carriers such as alumina, silica-alumina, silicon carbide, silicon nitride, titanium dioxide, aluminium sponge and the like.

[0019]

30 In this case, suitable supported ratio (%) of the complex oxide expressed by the general formula (1) ($\frac{\text{mass of the complex}}$

oxide) / (mass of the inert carrier + mass of the complex oxide)] x 100)
is 10-70%, preferably 15-50%.

[0020]

The complex oxide catalysts of the invention are obtained
5 upon calcination at a temperature of 300-600°C, preferably 350-500°C,
for 1-10 hours.

[0021]

Production of acrylic acid from acrolein according to the
present invention can be performed by heretofore known methods,
10 except that one of the so far described complex oxide catalysts should
be used as the catalyst. The apparatus and operating conditions in
carrying out the production are subject to no particular limitation.
That is, as the reactor, an ordinary fixed bed reactor, fluidable bed
reactor or moving bed reactor can be used. Talking about the reaction
15 conditions, the reaction can be carried out under the conditions
conventionally employed for production of acrylic acid from acrolein
through vapor phase catalytic oxidation reaction. For example, a
gaseous mixture of 1-15 volume % of acrolein, 0.5-25 volume % of
oxygen, 1-30 volume % of steam and 20-80 volume % of an inert gas
20 like nitrogen, is contacted with a complex oxide catalyst of the
invention at temperatures ranging from 200 to 400°C, under a
pressure of 0.1-1 MPa and at a space velocity of 300-5,000 h⁻¹ (STP) to
produce acrylic acid.

[0022]

25 Besides such gaseous mixtures of acrolein, oxygen and inert
gas, acrolein-containing gaseous mixtures which are obtained through
direct oxidation of propylene may also be used as the starting gas, if
necessary after adding air or oxygen and steam. Presence of such side
products as acrylic acid, acetic acid, carbon oxide and propane or
30 unreacted propylene in the acrolein-containing gaseous mixtures
obtained upon direct oxidation of propylene is in no way detrimental to

the catalysts used in the invention.

[0023]

[Effect of the invention]

According to the invention, high-activity and high-yield
5 catalysts are obtainable with good reproducibility. Moreover, because
the complex oxide catalysts of the invention maintain the high activity
levels over prolonged periods, acrylic acid can be stably produced at
high yields over prolonged periods according to the process of the
invention.

10 [0024]

[Examples]

Hereinafter the invention is explained more specifically
referring to working Examples, it being understood that the Examples
incur no restricting effect on the invention.

15 [0025]

In the Examples, the acrolein conversion, acrylic acid
selectivity and acrylic acid yield were calculated according to the
following formulae:

20 acrolein conversion (%) =
[(mol number of reacted acrolein) /
(mol number of fed acrolein)] x 100

acrylic acid selectivity (%) =
25 [(mol number of formed acrylic acid) /
(mol number of reacted acrolein)] x 100

acrylic acid yield (%) =
30 [(mol number of formed acrylic acid) /
(mol number of fed acrolein)] x 100

Example 1

[Preparation of Mg/Si-Al-containing compound]

Into 200 ml of pure water, 53 g of magnesium nitrate and 7.8 g of aluminium nitrate were dissolved under heating and stirring.

- 5 To this liquid 93 g of 20 mass % silica sol was added, mixed and evaporated to dryness under heating to provide a solid matter. The solid was heat-treated at temperatures elevated stagewise, followed by 3 hours' calcination finally at 1,400°C. The product was pulverized to a powder (1) having an average particle diameter of 30 μm .

10 [Preparation of catalyst]

- Into 2,000 ml of pure water, 350 g of ammonium paramolybdate, 106 g of ammonium metavanadate and 44.6 g of ammonium paratungstate were dissolved under heating and stirring. Separately, 87.8 g of cupric nitrate and 12 g of antimony trioxide were
- 15 added to 200 g of pure water under heating and stirring. Thus obtained two liquids were mixed, 11.2 g of the powder (1) was added to the liquid mixture and together poured into a porcelain evaporator on hot water bath. Then, 1,200 ml of a silica-alumina spherical carrier having an average particle diameter of 5 mm was added, followed by
- 20 evaporation to dryness under stirring to have the catalyst deposited on the carrier. The carrier-supported catalyst was calcined at 400°C for 6 hours to provide Catalyst (1). The composition of metallic elements (excepting oxygen, as in all of hereafter indicated compositions) of this Catalyst (1) was as follows:

25



The supported ratio was 23.4%.

[Oxidation reaction]

- 30 A stainless steel reaction tube of 25 mm in diameter was charged with 1,000 ml of thus obtained Catalyst (1), and into which a

gaseous mixture of 5 volume % of acrolein, 5.5 volume % of oxygen, 25 volume % of steam and 64.5 volume % of inert gas comprising nitrogen and the like was introduced. The reaction was carried out at 260°C and at a space velocity (SV) of 1,500 h⁻¹ (STP). The catalyst

- 5 performance at the initial period and after 8,000 hours' reaction was as shown in Table 1.

Comparative Example 1

- Catalyst (2) of the same composition to that of Catalyst (1) was prepared in the identical manner with Example 1, except that
- 10 "Mg/Si-Al-containing compound" was not prepared but the magnesium nitrate, silica sol and aluminum nitrate were used as they were. Using this Catalyst (2), the oxidation reaction was run under identical conditions with those of Example 1. The result was as shown in Table 1.

15 Example 2

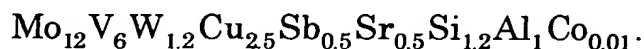
[Preparation of Sr/Si-Al-containing compound]

- To 74.4 g of 20 mass % silica sol, 10.7 g of strontium oxide, 0.6 g of cobalt nitrate and 10.5 g of aluminum oxide were added, mixed and evaporated to dryness under heating to form a solid matter. The
- 20 solid was heat-treated at temperatures elevated stagewise, and finally calcined at 1,500°C for 3 hours. Pulverizing the product, a powder (2) having an average particle diameter of 30 μm was obtained.

[Preparation of catalyst]

- Into 2,000 ml of pure water, 350 g of ammonium
- 25 paramolybdate, 116 g of ammonium metavanadate and 53.5 g of ammonium paratungstate were dissolved under heating and stirring. Separately, into 200 g of pure water, 99.8 g of cupric nitrate and 12 g of antimony trioxide were added under heating and stirring. The so formed two liquids were mixed, 28.9 g of the powder (2) was added,
- 30 and together poured into a porcelain evaporator on hot water bath. Then 1,200 ml of a silica-alumina spherical carrier having an average

particle diameter of 5 mm was added, followed by evaporation to dryness under stirring to have the catalyst deposited on the carrier. The carrier-supported catalyst was calcined at 400°C for 6 hours to provide Catalyst (3). The composition of the metallic elements in this
5 Catalyst (3) was as follows:



The supported ratio was 24.8%.

10 [Oxidation reaction]

The reaction was carried out under identical conditions with those in Example 1, except that Catalyst (1) was replaced with Catalyst (3). The result was as shown in Table 1.

Example 3

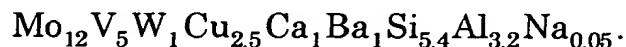
15 [Preparation of Ca-Ba/Si-Al-containing compound]

Into 200 ml of pure water, 48.8 g of calcium nitrate, 54 g of barium nitrate and 0.9 g of sodium nitrate were dissolved under heating and stirring. To this solution 335 g of 20 mass % silica sol and 33.7 g of aluminum oxide were added, mixed and evaporated to
20 dryness under heating to provide a solid matter. Thus obtained solid was heat-treated at temperatures elevated stagewise, and finally calcined at 1,400°C for 3 hours. Pulverizing the product, a powder (3) having an average particle diameter of 30 μm was obtained.

[Preparation of catalyst]

25 Into 2,000 ml of pure water, 350 g of ammonium paramolybdate, 96.6 g of ammonium metavanadate and 44.6 g of ammonium paratungstate were dissolved under heating and stirring. Separately, 99.8 g of cupric nitrate was dissolved in 200 g of pure water under heating and stirring. Thus formed two liquids were
30 mixed, to which 115.5 g of the powder (3) was added and together poured into a porcelain evaporator on hot water bath. Then 1,200 ml

of a silica-alumina spherical carrier having an average particle diameter of 5 mm was added and evaporated to dryness to have the catalyst deposited on the carrier, followed by 6 hours' calcination at 400°C to provide Catalyst (4). The composition of the metallic
5 elements of this Catalyst (4) was as follows:



The supported ratio was 26.7%.

10 [Oxidation reaction]

The reaction was carried out under identical conditions with those in Example 1, except that Catalyst (1) was replaced with Catalyst (4). The result was as shown in Table 1.

Example 4

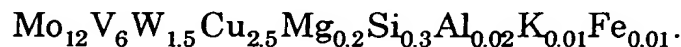
15 [Preparation of Mg/Si-Al-containing compound]

Into 400 ml of pure water, 12.7 g of magnesium nitrate, 0.2 g of potassium nitrate and 1.0 g of iron nitrate were dissolved under heating and stirring. Into this liquid 220 g of 20 mass % silica sol and 1.8 g of aluminum oxide were added, mixed and evaporated to dryness
20 under heating to provide a solid matter. The solid was heat-treated under temperatures raised stagewise, and finally calcined at 1,200°C for 3 hours. The product was pulverized to provide a powder (4) having an average particle diameter of 30 μm.

[Preparation of catalyst]

25 Into 2,000 ml of pure water, 350 g of ammonium paramolybdate, 116 g of ammonium metavanadate and 67 g of ammonium paratungstate were dissolved under heating and stirring. Separately, 99.8 g of cupric nitrate was dissolved in 200 g of pure water under heating and stirring. Thus formed two liquids were
30 mixed, and to which 186 g of the powder (4) was added and together put into a porcelain evaporator on hot water bath. Then 1,200 ml of a

silica-alumina spherical carrier having an average diameter of 5 mm was added, followed by evaporation to dryness under stirring to have the catalyst deposited on the carrier, followed by calcination at 400°C for 6 hours to provide Catalyst (5). The composition of the metallic
5 elements in this Catalyst (5) was as follows:



The supported ratio was 23.8%.

10 [Oxidation reaction]

The reaction was carried out under identical conditions with those in Example 1, except that Catalyst (1) was replaced with Catalyst (5). The result was as shown in Table 1.

Example 5

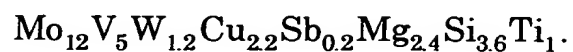
15 [Preparation of Mg/Si-containing compound]

One-hundred (100) g of magnesium silicate manufactured by Nakarai Tesqu Co. was calcined at 1,500°C for 3 hours to obtain a powder (5).

[Preparation of catalyst]

20 Into 2,000 ml of pure water, 350 g of ammonium paramolybdate, 96.6 g of ammonium metavanadate and 53.5 of ammonium paratungstate were dissolved under heating and stirring. Separately, 87.8 g of cupric nitrate, 13.0 of titanium dioxide and 4.8 g of antimony trioxide were added to 200 g of pure water under heating
25 and stirring. Thus obtained two liquids were mixed, 51.7 g of the powder (5) was added to the liquid mixture and together put into a porcelain evaporator on hot water bath. Then 1,200 ml of a silica-alumina spherical carrier having an average particle diameter of 5 mm was added and evaporated to dryness under stirring to have the
30 catalyst deposited on the carrier, followed by calcination at 400°C for 6 hours to provide Catalyst (6). The composition of the metallic

elements of this Catalyst (6) was as follows:



5 The supported ratio was 25.0%.

[Oxidation reaction]

The reaction was carried out under identical conditions with those in Example 1, except that Catalyst (1) was replaced with Catalyst (6). The result was as shown in Table 1.

[0026]

[TABLE I]

| | Catalyst No. | | Reaction Temp. (°C) | Acrolein conversion (%) | Acrylic Acid Selectivity (%) | Acrylic Acid Yield (%) |
|-----------------------|--------------|-----------------------------------------------|---------------------|-------------------------|------------------------------|------------------------|
| Example 1 | (1) | Initial stage of reaction After 8,000 hrs. | 260 268 | 99.1 99.2 | 96.0 95.8 | 95.1 95.0 |
| Comparative Example 1 | (2) | Initial stage of reaction After 8,000 hrs. | 260 291 | 97.0 97.8 | 93.8 93.1 | 91.0 91.1 |
| Example 2 | (3) | Initial stage of reaction After 8,000 hrs. | 260 267 | 99.6 99.4 | 95.6 95.4 | 95.2 94.8 |
| Example 3 | (4) | Initial stage of reaction After 8,000 hrs. | 260 272 | 99.0 99.0 | 95.4 95.3 | 94.4 94.3 |
| Example 4 | (5) | Initial stage of reaction After 8,000 hrs. | 260 271 | 99.0 99.2 | 95.8 95.7 | 94.8 94.9 |
| Example 5 | (6) | Initial stage of reaction After 8,000 hrs. | 260 274 | 99.1 99.0 | 95.2 94.9 | 94.3 94.0 |

[Document Name] ABSTRACT

[Abstract]

[Subject]

To provide ① a complex oxide catalyst which is particularly suitable for producing acrylic acid by vapor phase catalytic oxidation of acrolein and ② a process for producing acrylic acid by vapor phase oxidation of acrolein using this complex oxide.

[Means for solution]

① a complex oxide catalyst represented by the following general formula (1): $\text{Mo}_a\text{V}_b\text{W}_c\text{Cu}_d\text{A}_e\text{B}_f\text{C}_g\text{D}_h\text{E}_i\text{O}_x$ (in which Mo is molybdenum; V is vanadium, W is tungsten, Cu is copper, A is at least an element selected from antimony, niobium and tin; B is at least an element selected from alkaline earth metals; C is at least an element selected from silicon, aluminum, titanium and zirconium; D is at least an element selected from phosphorus, tellurium, cerium, lead, arsenic and zinc; E is at least an element selected from Group IA and Group IIb elements of the periodic table, boron, iron, bismuth, cobalt, nickel and manganese; and O is oxygen; a, b, c, d, e, f, g, h, i and x denote the atomic ratios of Mo, V, W, Cu, A, B, C, D, E and O, respectively; and where $a = 12$, $2 \leq b \leq 15$, $0 \leq c \leq 10$, $0 < d \leq 6$, $0 \leq e \leq 6$, $0 < f \leq 10$, $0 < g \leq 10$, $0 \leq h \leq 5$, $0 \leq i \leq 5$, and x is a numerical value determined by the extents of oxidation of the other elements) which is prepared by using, as at least a part of the supply sources of components B and C, a compound containing both of the components B and C; ② production of acrylic acid by vapor phase oxidation of acrolein in the presence of this complex oxide catalyst.

[Selected drawing] None